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COMPLETE SPECIFICATION

U. S. PATENT OFFICE

Process for Manufacturing Minute Capsules having Waxy Material Walls

We, THE NATIONAL CASH REGISTER COMPANY of Dayton in the State of Ohio, and Baltimore in the State of Maryland, United States of America, a Company organized under the laws of the State of Maryland, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of manufacturing minute capsules, particularly capsules having nuclei of oil-immiscible material invested with seamless conforming walls of heat-liquefiable waxy material.

The process is carried out in a hot oily vehicle into which wax-like wall materials, either unliquefied or preliquefied, and nucleus materials are introduced to form a three-phase system, the oily vehicle being a continuous phase and the waxy wall material and nucleus materials being two interspersed phases. The system is kept agitated, so that the wax, which is liquefied by the heat, is broken up into small entities, which coat the nucleus material particles to form waxy liquid-walled capsules. Thereafter, with continued agitation, the system is cooled to set the walls to a solid condition to complete the capsules, after which they may be recovered and used as desired.

Such capsules are useful individually to protect the nucleus material from various environments, to act as a component of a mixture of capsules having different nucleus materials which may be reactive on contact when the capsule walls are broken, to provide pseudo-dry liquids when the nuclei are liquid, to provide taste masking for drugs, and many other purposes which will be evident from what is to follow.

These capsules may range in size from one to one thousand or more microns, depending on the capsule nucleus material selected for use. If solids are used, greater dimensions may be obtained.

The only conditions in the selection of materials are that they must be mutually immiscible, that they do not react with each other and that the waxy material is a solid at room temperature, deposits on the nucleus material, as most waxy liquid materials do, and melts in the chosen vehicle. The nucleus material may be liquid or solid, or mixtures of liquid and solid materials. It may also be a suspension of solid particles in a liquid. If the waxy material melts below 100 degrees Centigrade, water may be encapsulated.

It is within the scope of the invention to provide systems wherein more than one kind of nucleus material is used, which may be different in composition or in physical state. The nucleus material is introduced into the system either as a particulate solid or as a liquid which is reduced by the agitation to the desired drop size, the agitation being controlled in any manner to achieve this end. The nucleus material may be solid at room temperature and a liquid at the liquefying temperature of the wax.

The order of introduction of the materials into the vessel is not critical. Thus:—

1. The nucleus material may be added to the vehicle already containing the wax;
2. the wax may be added to the vehicle already containing the nucleus material;
3. a dispersion of vehicle and wax may be added to a dispersion of vehicle and nucleus material;
4. a slurry of liquefied wax and nucleus material; or
5. the wax and the nucleus material may have the vehicle added thereto.

If the ingredients are cold when added together, they may later be heated to manufacturing temperature. The mixture of ingredients may be stored cold for later use, provided that the materials are not affected by aging or prolonged contact with each other or the environment. The atmospheric environment may be excluded by canning the mixture for future use.

The dispersed materials should not be crowded into the manufacturing vehicle to a point where agglomeration occurs.

It has been found that, preferably, there should be at least five times the amount of liquid vehicle as there is dispersed material, by volume. So afford complete freedom of movement of the dispersed material, and that the ratio of nucleus material to wax should be in the range of from 1:10 to 10:1, depending on the amount of nucleus particle surface to be covered and the desired wall thickness to be deposited.

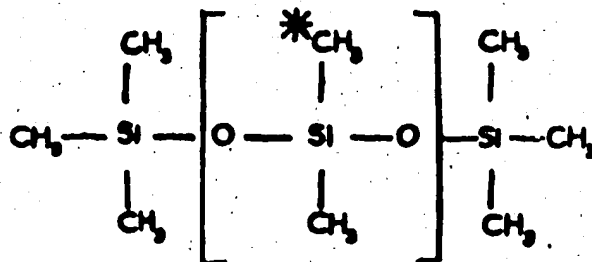
Thus, according to the invention there is provided a process for manufacturing minute capsules enclosing a liquid and/or solid nucleus material including the steps of providing a heated and agitated three-phase system consisting of a continuous phase of a substantially inert oil having therein two discontinuous phases, one being of a nucleus material and the other of a waxy wall-forming material, said materials being mutually non-reactive, and the waxy material being liquid in the heated system but solid at room temperature and being capable of depositing on contact on each entity of the nucleus material to form liquid walls therearound, and cooling the system with continued agitation until the liquid waxy capsule walls become solidified.

A preferred embodiment of the process according to the invention will now be described by way of example. Into 500 grams of silicone oil (referred to hereinafter as Compound III), having a viscosity of 475 to 525 centistokes at 25 degrees Centigrade, is dispersed 5 grams of polyethylene having a sharp melting point of about 130 degrees Centigrade, a density of 0.92 to 0.95, and a molecular weight of about 2500, the temperature of the oil being maintained above the melting point of the polyethylene, and the system being agitated until the drop size of the melted polyethylene comes to approximately 100 microns. Into this system is introduced, at any time during the foregoing operations, particles of ammonium nitrate of a particle size of 250 microns. The liquid polyethylene will deposit on the particles to form liquid waxy walled capsules. The agitation is continued while the system is allowed to cool to room temperature to solidify the walls. The finished capsules may then be recovered from the oily vehicle by conventional methods of decantation, filtration, centrifuging, and the like, or they may be used in the vehicle in which they were manufactured.

Typical waxy materials are the sharp melting point polyethylenes and alkyl straight-chain and branched derivatives thereof, which are solid at room temperature (20 to 25 degrees Centigrade). Other materials that may be used are Carnauba wax, spermaceti wax, and a great variety of synthetic and natural waxes, preferably with sharp melting points. Microcrystalline wax may be mentioned specifically among the mineral waxes. Mixtures of waxes may be used. Other waxes useful in practicing the invention are beeswax, candelilla wax, paraffin wax, montan wax, Japan wax, and the like.

The oils which may be used as the manufacturing vehicle are water-immiscible liquids, generally soluble in ether, which are substantially inert to the wall-forming and nucleus materials, and the term "oil" and "oily vehicle" as used in the specification and the appended claims are meant to indicate such liquids. The oily vehicles that have been found most suitable are

I. A fluid silicone compound having the structure



and having a decomposition range of 250 to 300 degrees Centigrade.

II. The compound of I in which 25% of the CH_3 substituents are replaced by phenyl groups, such compound having a decomposition range of 350 to 400 degrees Centigrade.

III. The compound of I in which 100% of the $*\text{CH}_3$ substituents are replaced

by phenyl groups, such compound having a decomposition range of 450 to 500 degrees Centigrade.

IV. Tributyl amine (C_4H_9)₃N in which the hydrogen has been replaced by fluorine having a boiling point of 170 to 180 degrees Centigrade, and isomers thereof.

V. A mixture of perfluoro cyclic ether isomers ($C_4F_{10}O$) having a boiling point range of 100 to 110 degrees Centigrade.

It will be observed that all of these compounds except Compounds I, II, and III are fluorine substituted, and all of them are practically inert to any waxy material or any nucleus material that it is desired to encapsulate. This does not preclude the use of oily vehicles that have some reactivity if used with waxy wall material and nucleus material non-reactive therewith, and the invention is not to be deemed limited to silicone oils or fluorinated oily materials. Mixtures of the oily vehicles may be used as the occasion demands, for special temperature conditions.

In the following a list is given of chemically compatible, mutually immiscible materials which proved to be particularly suitable combinations for the purposes of the invention.

Nucleus Material	Wall Material	Manufacturing Vehicle
Magnesium Hydride	Polyethylene	I, II, III
Ammonium Nitrate	Polyethylene	I, II, III, IV
Potassium Dichromate	Polyethylene	I, II, III, IV
Ammonium Dichromate	Polyethylene	I, II, III, IV
Aspirin	Polyethylene	I, II, III, IV
d-Propoxyphene . HCl	Polyethylene	I, II, III, IV
Quinidine Gluconate	Paraffin	IV
Cadmium Borate	Polyethylene	I, II, III, IV
Aspirin	Tristearin	IV
Aspirin	Diglyceride	IV
Ammonium Dichromate	Tristearin	IV
d-Propoxyphene . HCl	Tristearin	IV
Sodium Bicarbonate	Paraffin	IV
Sodium Bicarbonate	Tristearin	IV
Stannous Fluoride	Tristearin	IV
Stannous Fluoride	Paraffin	IV
Stannous Fluoride	Polyethylene	IV
Bitoluene 4,4 - Dithiocyanate	Japan Wax	IV
Toluene Dithiocyanate	Paraffin	IV
Toluene Dithiocyanate	Polyethylene	IV
Diphenylmethane 4,4 - Dithiocyanate	Paraffin	IV

Nucleus Material	Wall Material	Manufacturing Vehicle
Diphenylmethane 4,4 - Diisocyanate	Paraffin — 5% Vinyl Resin	IV
Ammonium Nitrate	Polyethylene (Metal Particles)	
Diphenylmethane 4,4 - Diisocyanate	Japan Wax	IV
Diphenylmethane 4,4 - Diisocyanate	Cerita Wax	IV
Sodium Dichlorocyanurate	Polyethylene	I, II, III
Potassium Dichlorocyanurate	Polyethylene	I, II, III
Chlorinated Trisodium Phosphate	Polyethylene	I, II, III
Azodicarbonamide (Blowing Agent)	Polyethylene	I, II, III, IV
Diethylenetriamine	Paraffin/20% Vinyl Resin	IV

This list is exemplary only, and is in no way to be deemed a limitation as to the broad aspects of the invention. The polyethylenes range from 2,500 to 12,000 in molecular weight. The reference in the above list to metal particles pertains to the introduction of such as powder, to the vehicle, after the liquid waxy walls have been formed. Such material becomes adherent to the walls and is maintained thereafter the cooling and hardening thereof. Aluminum powder is typical, but any dispersable powder of non-reactive nature can thus be deposited in the capsule walls while they are still in a liquid state. Other examples are colloidal silica, magnetic iron oxide, iron powder, and the like. The powdered materials may act as insulators, electrical or electrostatic materials, chemical powders that are reactant with the capsule contents, etc. The vinyl resin used was a copolymer of ethylene and vinyl acetate.

It is evident that the capsules made by the method disclosed herein may be used as nuclei for the reception of an overcoating of another material of waxy characteristics or of hydrophobic or hydrophilic polymers applied by methods known in the art.

WHAT WE CLAIM IS:—

1. A process for manufacturing minute capsules enclosing a liquid and/or solid nucleus material including the steps of providing a heated and agitated three-phase system consisting of a continuous phase of a substantially inert oil having therein two discontinuous phases, one being of a nucleus material and the other of a waxy wall-forming material, said materials being mutually non-reactive, and the waxy material being liquid in the heated system but solid at room temperature and being capable of depositing in contact on each entity of the nucleus material to form liquid walls therearound, and cooling the system with continued agitation until the liquid waxy capsule walls become solidified.

2. A process according to Claim 1, wherein the ratio of nucleus material to waxy material ranges from 1:10 to 10:1.

3. A process according to Claim 1 or 2, wherein a non-reactive powdered material is added to the system after the liquid waxy walls have been formed.

4. A process for manufacturing minute capsules substantially as hereinbefore described.

E. T. BEAVIS,
Agent for the Applicants.

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